both benzene and toluene labeled with C^{14}. Earlier work has shown that C^{14} produced by the N^{14} $(n,p)C^{14}$ reaction is able to substitute for C and for N atoms in compounds such as acridene,[30] and pentane.[31] All of these reactions, like the halogen reactions described in the present paper, have been difficult to explain in terms of available theories of reactions activated by nuclear processes and it appears that a good working hypothesis is that they all involve steps of the ion-molecule type.

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MADISON, WISCONSIN

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[30] A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955).

[31] A. G. Schrodt and W. F. Libby, *ibid.*, **76**, 971 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Tetrakistriphenylsiloxytitanium and Some Related Compounds[1]

BY VERNON A. ZEITLER AND CHARLES A. BROWN[2]

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Tetrakistriphenylsiloxytitanium was prepared in good yield by the reaction of triphenylsilanol with tetrabutoxytitanium and by the reaction of triphenylsilanol with titanium tetrachloride in the presence of ammonia. This compound shows an unusually high melting point, 501–505°, and possesses considerable inertness toward acids and bases. Some physical and chemical properties are discussed. Related compounds such as tetrakistriphenylsiloxysilane, tetrakistrimethylsiloxysilane are described and some properties of the compound triphenylbutoxysilane are given.

Prior to 1955 no silicon–oxygen–titanium molecular type compound had been reported in the literature. Titanated siloxanes[3] have been mentioned, but no information was given as to the compositions or the properties associated with the siloxy groups attached to titanium. In 1955 English and Sommer[4] described the preparation of $[(CH_3)_3SiO]_4Ti$ by the reaction of the appropriate silanol with titanium tetrachloride.

Calculations of bond strengths indicate that the Ti–O bond (~112 kcal./mole) should be approximately the same strength as the Si–O bond (~103 kcal./mole). In addition it has been shown that Si–C bonds are somewhat resistant to hydrolysis and that phenyl groups attached to silicon exhibit greater thermal stabilities than the alkyl silicon derivatives. As a consequence, the preparation of phenylsiloxy derivatives of titanium was undertaken with the hope of preparing substances of moderate to high thermal and chemical stability.

Experimental

Since the chlorides and esters of titanium and silicon hydrolyze readily, adequate precautions were taken to prevent exposure of these substances to water. Necessary operations were carried out in a dry atmosphere. All solvents were dried by means of an appropriate desiccant and distilled, or dried by azeotropic distillation. Tetra-*n*-butyl titanate from the Pigments Department, E. I. du Pont de Nemours Co., Inc., was purified by fractional distillation (b.p. 139–140° at 2 mm.). Tetraethoxysilane, Distillation Products Industries, was fractionally distilled (b.p. 165–167°). Titanium tetrachloride was of C.P. grade from Fisher Scientific Co. The triphenylsilanol was of purified (98%) grade.

Tetrakistriphenylsiloxytitanium

Preparation of $[(C_6H_5)_3SiO]_4Ti$. Method 1.—The reaction of triphenylsilanol with tetrabutoxytitanium was carried out, both in benzene and without solvents. The products were *n*-butyl alcohol and tetrakistriphenylsiloxytitanium, according to the equation

$$Ti(OC_4H_9)_4 + 4(C_6H_5)_3SiOH \longrightarrow 4C_4H_9OH + [(C_6H_5)_3SiO]_4Ti$$

When an excess of triphenylsilanol was used, triphenylbutoxysilane, a new compound, was also a product. Otherwise the reaction is essentially quantitative with respect to the formation of the above products. Variations in the mole ratios of reactants *did not* give partially substituted titanium esters.

In a typical preparation, equal molar quantities of tetrabutoxytitanium and triphenylsilanol were mixed. The reaction was slow, but quantitative amounts of *n*-butyl alcohol were recovered by distillation from the mixture. The *n*-butyl alcohol was identified by its refractive index.

The addition of tetrabutoxytitanium to a benzene solution of triphenylsilanol resulted in an instantaneous formation of a white precipitate as the desired product. In one reaction, 0.12 mole of tetrabutoxytitanium was treated with 0.60 mole of triphenylsilanol in one liter of benzene. The crude product (0.12 mole) was removed by filtration. Distillation of the filtrate to remove solvent also yielded 0.12 mole of triphenylbutoxysilane.

Method 2.—Tetrakistriphenylsiloxytitanium has also been prepared by the method of English and Sommer, according to the equation

$$TiCl_4 + 4(C_6H_5)_3SiOH + 4NH_3 \longrightarrow 4NH_4Cl + [(C_6H_5)_3SiO]_4Ti$$

$TiCl_4$ (0.1 mole), dissolved in 25 ml. of dry benzene, was added dropwise to 0.2 mole of triphenylsilanol dissolved in 1500 ml. of dry benzene. The apparatus consisted of a three-neck, three-liter flask equipped with a Trubore stirrer, reflux condenser and an ammonia delivery tube coaxial with the condenser. The flask was cooled in an ice-bath during the addition of the titanium tetrachloride. The ammonia was bubbled through the solution from the start of the $TiCl_4$ addition to the beginning of reflux. A strong yellow color developed. This color disappeared with the further addition of 0.22 mole of triphenylsilanol. The solution was refluxed for several hours to remove the ammonia and then filtered. The precipitate was washed with benzene, acetone and finally with water to remove the ammonium chloride. The white product was dried and purified by vacuum sublimation at 370°. Soxhlet extraction of impure tetrakistriphenylsiloxytitanium is an effective, but slow, method of purification.

Properties of $[(C_6H_5)_3SiO]_4Ti$.—Tetrakistriphenylsiloxytitanium is only slightly soluble in benzene, toluene, chloro-

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[1] Presented before the Division of Physical and Inorganic Chemistry, 128th meeting, ACS, Minneapolis, Minnesota, September 14, 1955. Taken from the thesis of V.A.Z. submitted in partial fulfillment of the requirements for the Ph.D. degree, 1956.

[2] Advance Development Laboratory, Lamp Wire and Phosphors Department, General Electric Company, Cleveland 10, Ohio.

[3] H. C. Gulledge, U. S. Patent 2,512,058 (June 20, 1950).

[4] W. D. English and L. H. Sommer, THIS JOURNAL, **77**, 170 (1955).

benzene and nitrobenzene at their boiling points. It is insoluble in methyl alcohol, ethyl alcohol, diethyl ether, acetone, carbon disulfide and carbon tetrachloride. It reacts with N,N-dimethylformamide and camphor. It does not appear to react, even on heating with 0.1 *N* sodium hydroxide, dilute hydrochloric acid or dilute sulfuric acid. It does not react with hot concentrated HCl, but does react with concentrated sulfuric and nitric acids. It is non-hygroscopic when exposed to atmospheres of high humidity. The slight gain in weight is lost readily when stored in a desiccator over phosphorus pentoxide. Much of the inert character of the compound may be due to its resistance to wetting.

Either crystallization from solution or sublimation produces very soft, colorless, hexagonal crystals with an index of refraction at 114–115° of 1.6488. The index of refraction was determined on a hot-stage microscope, using N-phenyl-α-naphthylamine as the immersion liquid. The crystals melt with decomposition at 501–505° in sealed evacuated tubes as measured with a chromel–alumel thermocouple in a hot copper block. The crystals decompose in open tubes between 460 and 470°. The density of the crystals is 1.215 g./cc. at 29° as determined in a pycnometer by the displacement of a saturated toluene solution.

Analyses.—Two methods were used to free the titanium and silicon for analyses. In the first method, fusion with sodium peroxide and finely divided carbon[5] in the ratio of 12:1 in a nickel crucible had the advantage of liberating the titanium in a usable form. The solution was free of nickel and was suitable for colorimetric methods, since there was no interference by partially oxidized carbon compounds. However, silicon analyses were consistently low. The button, resulting from the fusion, was dissolved in water and acidified with sulfuric acid. Titanium was determined colorimetrically at 420 mμ using 30% hydrogen peroxide to develop the color.[6] The p.p.m. of titanium present was determined by comparison of the per cent. transmission with a reference curve obtained from standard solutions.

The second method for cracking the titanium–silicon compound consisted of heating the sample with concentrated sulfuric acid and ammonium sulfate for two hours. The resulting solution was diluted, filtered and the precipitated silica ignited. Nitric acid cannot be used with phenyl–silicon bonds due to tar and wax formation. Because of the incomplete oxidation of the carbon compounds, the colorimetric method could not be used to determine titanium. Hydrated titanium oxide was precipitated and the dioxide weighed.

Anal. Calcd. for $[(C_6H_5)_3SiO]_4Ti$: Ti, 4.17; Si, 9.76; C, 75.26; H, 5.23. Found: Ti (colorimetric), 4.11, 4.15, 4.20, 4.43; Ti (grav.), 4.44; Si, 9.82, 9.72; C, 75.28; H, 4.87.

Molecular Weight.—Cryoscopic methods failed in the usual solvents due to the very low solubility of the compound at the freezing points. The Rast method could not be used due to the reaction of the compound with camphor. Satisfactory molecular weight measurements were made using an ebulliometer and differential vapor pressure thermometers. The ebulliometer was similar to the design of Kitson[7] but was modified to provide heating by induction.[8] In benzene solutions the compound gave molecular weight values of 1212 and 1187 (calcd. 1149.5). Triphenylsilanol was used as the standard for the determinations.

Triphenylbutoxysilane

Preparation and Properties of $(C_6H_5)_3SiOC_4H_9$.—Triphenylbutoxysilane, a new compound, was identified as a by-product of the transesterification reaction when an excess of triphenylsilanol was used. Triphenylbutoxysilane is a pale yellow liquid, b.p. 141–145° at 1 mm. It crystallizes slowly at room temperature to a hard, pale cream-colored solid with an m.p. of 53–53.5°.

The direct preparation of the compound was accomplished according to the reaction

$$(C_6H_5)_3SiCl + C_4H_9OH + NH_3 \longrightarrow (C_6H_5)_3SiOC_4H_9 + NH_4Cl$$

Triphenylchlorosilane, 0.14 mole, dissolved in 500 ml. of dry benzene, was placed in a three-neck, one-liter flask equipped with a mercury-seal stirrer, reflux condenser, ammonia delivery tube coaxial with the condenser, and a dropping funnel. The condenser and the dropping funnel were protected by drying tubes filled with Drierite. Butyl alcohol, 0.19 mole, was placed in the dropping funnel and added slowly over a period of two hours with vigorous stirring. Ammonia was bubbled through the reaction flask from the beginning of the addition of the alcohol until the start of reflux. No evolution of heat was detected during the addition. The mixture was refluxed for two hours, cooled and filtered rapidly in an atmosphere of dry nitrogen. The ammonium chloride was washed with dry benzene and the filtrate and washings were combined. The benzene and excess butyl alcohol were removed by distillation, the final portion of alcohol being removed at reduced pressure. The product distilled at 145–148° at about 1 mm. A yield of 20.5 g. (44% yield based on the amount of triphenylchlorosilane available) was obtained. No hexaphenyldisilazane was found.

The production of triphenylalkoxysilanes, when an excess of triaryl- or trialkylsilanol is treated with tetrabutoxytitanium, suggests that the titanium ester aids in the reaction of the silanol with the butoxy group. Triphenylbutoxysilane and trimethylbutoxysilane were identified as by-products in reactions where the respective silanols reacted in excess with tetrabutoxytitanium. Triphenylbutoxysilane was *not* produced when triphenylsilanol and butyl alcohol were refluxed alone or in the presence of tetrakistriphenylsiloxytitanium.

Analyses and Molecular Weight.—Molecular weights were determined in benzene by means of the ebulliometer. Hexaphenyldisiloxane was used as the reference. Experimental: 353, 358, 327, 349; calcd.: 332.

Anal. Calcd. for $(C_6H_5)_3SiOC_4H_9$: Si, 8.43; C, 79.50; H, 7.23. Found: Si, 8.45, 8.46; C, 79.62; H, 7.17.

Tetrakistrimethylsiloxytitanium

Tetrakistrimethylsiloxytitanium was prepared by a transesterification reaction between trimethylsilanol and tetrabutoxytitanium in 56% yield as compared to the 18% yield secured by English and Sommer in the reaction of $TiCl_4$ with trimethylsilanol in the presence of ammonia.

Preparation of $[(CH_3)_3SiO]_4Ti$.—Trimethylsilanol was prepared by the method reported by Sauer[9] from hexamethyldisilazane. Trimethylsilanol, 0.755 mole, was dissolved in 500 ml. of toluene, previously dried over calcium hydride, and placed in a one-liter, three-neck flask equipped with Trubore stirrer, reflux condenser and a dropping funnel. Tetrabutoxytitanium, 0.1 mole, dissolved in 150 ml. of dry toluene, was added slowly from the dropping funnel over a period of two hours to the well-stirred silanol solution. The mixture was refluxed two hours and then distilled. Following the butyl alcohol–toluene azeotrope, toluene was removed. The last portion of toluene and a small amount of trimethylbutoxysilane (b.p. 124°)[10] was recovered prior to reduction of the pressure. After the last portion of the trimethylbutoxysilane was removed, 22.6 g. of tetrakistrimethylsiloxytitanium was recovered, b.p. 102–106° at 5–7 mm. (106° at 7 mm.[4]). This distillate represents a yield of 56% based on the amount of titanium available.

Tetrakistriphenylsiloxysilane

The marked differences of tetrakistrimethylsiloxytitanium and tetrakistrimethylsiloxysilane[11] suggested the need for the preparation of tetrakistriphenylsiloxysilane, a new compound, for comparison with tetrakistriphenylsiloxytitanium. The following different methods for the preparation of tetrakistriphenylsiloxysilane were tried

$$4(C_6H_5)_3SiONa + SiCl_4 \longrightarrow [(C_6H_5)_3SiO]_4Si + 4NaCl \quad (a)$$

$$4(C_6H_5)_3SiOH + (C_2H_5O)_4Si + 4Na \longrightarrow [(C_6H_5)_3SiO]_4Si + 2H_2 + 4C_2H_5ONa \quad (b)$$

$$SiCl_4 + 4(C_6H_5)_3SiOH \xrightarrow{\text{pyridine}} [(C_6H_5)_3SiO]_4Si + 4HCl\ (\text{pyridine}) \quad (c)$$

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(5) S. Y. Tyree, Jr., University of North Carolina, private communication.

(6) C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, VIII-1, p. 471.

(7) R. E. Kitson and J. Mitchell, Jr., *Anal. Chem.*, **21**, 401 (1949).

(8) A description will soon appear elsewhere.

(9) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

(10) E. G. Rochow, "An Introduction to the Chemistry of Silicones," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 180.

(11) L. H. Sommer, L. Q. Green and F. C. Whitmore, THIS JOURNAL, **71**, 3253 (1949).

TABLE I

SOME PROPERTIES OF ANALOGOUS SILICON AND TITANIUM DERIVATIVES

	$[(CH_3)_3SiO]_4Si$	$[(CH_3)_3SiO]_4Ti$	$[(C_6H_5)_3SiO]_4Si$	$[(C_6H_5)_3SiO]_4Ti$
M.p., °C.	−60	.....	235	501–5
B.p., °C.	91 (9 mm.) 220 (733 mm.)	106 (7 mm.)	249 (1 mm.)	Subl. 370 (1 mm.)
Density	0.8677 (20°)	0.9078 (20°)	....	1.215 (29°)
Ref. index	1.3895 (20°)	1.4278 (20°)	....	1.6488 (114°)
Sol. in benzene	Very sol.	Very sol.	Very sol.	Very slightly sol.

In each case, the desired product was obtained but method (a) proved to be the best method and is the only one described below. It should be noted that a transesterification reaction was not successful.

Preparation of $[(C_6H_5)_3SiO]_4Si$.—Triphenylsilanol, 0.257 mole, dissolved in 750 ml. of dry toluene, was placed in a two-liter, three-neck flask. The flask was equipped with a Trubore stirrer, reflux condenser and a dropping funnel. Freshly cut sodium, 0.25 mole, was added in small pieces. The evolution of hydrogen was slow until the temperature was raised to the melting point of sodium. The triphenylsiloxysodium precipitated as a fine white powder[12] upon cooling. Then $SiCl_4$, 0.075 mole, in 50 ml. of dry toluene, was placed in the dropping funnel and added slowly over a period of two hours to the vigorously stirred mixture. The resulting mixture was refluxed 30 hours. On cooling, a heavy deposit of crystals formed on the stirrer and on the walls above the fine deposit of NaCl. The cold solution was filtered and the residue washed with two 250-ml. portions of dry toluene. The washings and filtrate were combined and distilled to recover the bulk of the tetrakistriphenylsiloxysilane which is more soluble in toluene and benzene than hexaphenyldisiloxane. The residue was dried and purified by fractional crystallization. Some hexaphenyldisiloxane was observed in the residue.

Analysis and Molecular Weight.—Samples were heated with concentrated sulfuric acid and ammonium sulfate. The resulting mixture was cooled, diluted with water and filtered. The residue was ignited and weighed as SiO_2.

Anal. Calcd. for $[(C_6H_5)_3SiO]_4Si$: Si, 12.42. Found: Si, 12.26, 12.30.

The molecular weight was determined in the ebulliometer in benzene with hexaphenyldisiloxane as the reference; mol. wt. found, 1128, 1115; calcd., 1129.5.

Properties.—The compound is a colorless, crystalline solid, m.p. 235–235.5°. It is very soluble in benzene and toluene and has limited solubility in carbon disulfide. In open tubes, different samples appeared to have boiling points between 310 and 330°. In evacuated, sealed tubes, the boiling point was about 249°. At 490–510° the liquid appeared to undergo a change, becoming more viscous, but no color developed until 539°. At 605°, the liquid was very viscous and a pale yellow in color. In comparison, a sample of hexaphenyldisiloxane in an open tube was colorless at 532°.

Discussion

At first it might be expected that the thermal stabilities of Si–O–Si and Ti–O–Si compounds should be somewhat similar in that the Ti–O and Si–O bonds are of almost the same strength. Comparison of the thermal decompositions of the tetrakistriphenylsiloxy derivatives of titanium and silicon clearly indicated a greater degree of stability for the silicon compound. The titanium compound turned brown around 460–470° whereas the silicon compound showed little change even at 605°. In addition, the titanium compound gave a dark color indicating carbonization. Apparently the introduction of Ti–O bonds for some Si–O bonds has a wakening effect on neighboring Si-C bonds.

A comparison of a few properties of these substituted silicon and titanium compounds (Table I) reveals the unusually high melting point of tetrakistriphenylsiloxytitanium. The effect does not seem to be due to just the presence of titanium or to the phenyl groups.

It has been observed that this compound has low solubility in benzene and toluene; whereas the corresponding phenylsiloxy derivative of silicon has relatively high solubility in the same solvents. These differences suggest that tetrakistriphenylsiloxytitanium may not be monomeric in the solid state. The ebulliometer measurements gave molecular weights slightly above the values calculated for the monomer. It was not determined whether this difference is a real effect or is due to experimental error. Since titanium exhibits a coördination number of six whereas silicon usually observes a coördination number of four, it is possible that a molecule of the titanium compound might coördinate through the siloxy oxygen to a neighboring molecule.

Acknowledgment.—We wish to acknowledge gratefully the support of the Office of Naval Research during the major portion of this research.

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[12] W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

The Reactions of Triphenylsilanol and Diphenylsilanediol with Some Titanium Esters[1]

BY VERNON A. ZEITLER AND CHARLES A. BROWN[2]

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The reaction of triphenylsilanol with condensed esters of titanium leads to rupture of the Ti–O–Ti bonds with the formation of tetrakistriphenylsiloxytitanium. In addition, triphenylsilanol reacts with chloroesters of titanium in a similar fashion to yield the same product. Diphenylsilanediol and *n*-butyl titanate give an unusual spiro compound of the composition $Ti[O_5Si_4(C_6H_5)_8]_2$. Evidence for the composition and structure of this substance is presented.

In the preceding paper,[3] it was reported that triphenylsilanol and tetrabutoxytitanium react quantitatively to give tetrakistriphenylsiloxytitanium. This product has an unusually high melting point and chemical inertness. In an attempt to prepare stable materials of even higher molecular weight, reactions were carried out to prepare materials containing Ti–O–Ti bonds. Due to the stability of the triphenylsiloxy group, blocking of the remaining primary valences of titanium by these groups should lead to either simple molec-

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[1] Taken from the Ph.D. thesis of V. A. Zeitler, February, 1956.

[2] Advance Development Laboratory, Lamp Wire and Phosphors Department, General Electric Company, Cleveland 10, Ohio.

[3] V. A. Zeitler and C. A. Brown, THIS JOURNAL, **79**, 4616 (1957).